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## **Preparation of Nanosized Non-Oxide Powders Using Diatomaceous Earth**

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### **Abstract:**

*In this paper the nanosized non-oxide powders were prepared by carbothermal reduction and subsequent nitridation of diatomaceous earth which is a waste product from coal exploitation. Our scope was to investigate the potential use of diatomaceous earth as a main precursor for low-cost nanosized non-oxide powder preparation as well as to solve an environmental problem. The influence of carbon materials (carbonized sucrose, carbon cryogel and carbon black) as a reducing agent on synthesis and properties of low-cost nanosized nonoxide powders was also studied. The powders were characterized by specific surface area, X-ray and SEM investigations. It was found that by using diatomaceous earth it is possible to produce either a mixture of non-oxide powders ( $\text{Si}_3\text{N}_4/\text{SiC}$ ) or pure SiC powders depending on temperature.*

**Keywords:** Gas-solid reactions; Microstructure; X-ray diffraction; Scanning electron microscopy

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## **1. Introduction**

Near Belgrade there is a huge basin of diatomaceous earth (Kolubara basin, approximately, 1 206 667 tons). This basin has layers of diatomaceous earth. During the exploitation of coal a huge amount of diatomaceous earth is deposited. Diatomaceous earth is a natural occurring mineral compound developed from microscopic siliceous skeletal remains of unicellular algae-like plants called diatoms. Diatomaceous earth has already been successfully used as Si precursor for obtaining pure SiC and  $\text{Si}_3\text{N}_4$  [1-3]. However, by our best knowledge, no work has been done on in situ synthesis of a mixture of non-oxide powders ( $\text{Si}_3\text{N}_4/\text{SiC}$ ) from inexpensive raw materials which should have a number of advantages compared to pure powders due to its low-cost, narrow particle size and ideal homogeneity.

Phase evolution during carbothermal reaction was also followed in three reacting mixtures differing in the carbon precursor component (carbonized sucrose, carbon cryogel and carbon black). One of the goals of this work was to find the conditions under which composite materials can be synthesized starting with diatomaceous earth as  $\text{SiO}_2$  precursor and carbon precursors of different origin.

Silicon nitride ( $\text{Si}_3\text{N}_4$ ) and silicon carbide (SiC) are important structural materials because of their unique combination of properties, such as high temperature strength, thermal

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shock resistance, high fracture toughness and resistance to wear and corrosion [4]. Because of this,  $\text{Si}_3\text{N}_4$  and SiC, respectively, have been major candidate materials for widespread use in engineering applications. The synthesis of pure powders is one of the important factors for obtaining dense  $\text{Si}_3\text{N}_4$  and SiC ceramics [5]. Although the quality and performance are important, the cost of mass production should be the key factor in the commercialization of  $\text{Si}_3\text{N}_4$  and SiC ceramics [6]. A ceramic nanocomposite concept allows improvement of high-temperature strength and creep resistance in comparison with the pure ceramic components [7]. Different processing techniques have been applied for the preparation of  $\text{Si}_3\text{N}_4$ /SiC composites [8, 9]. In most cases the mixing of two powders ( $\text{Si}_3\text{N}_4$  and SiC) and their sintering is the common technique. However, the problem with homogenization is always present. Better solution might be to use the composite powders obtained in situ.

The process known as carbothermal-nitridation during which mixtures of siliceous and carbonaceous materials in general react under  $\text{N}_2$ ,  $\text{N}_2/\text{H}_2$  or  $\text{NH}_3$  atmospheres at temperatures above 1273 K is the most promising candidate for obtaining a wide variety of non-oxide products for important technical application [10]. This reaction offers the possibility of an economically attractive production route starting with naturally occurring materials which are inexpensive. Many authors studied the formation of non-oxide powders from various minerals such as different types of clays [11-16]; sepiolite [17], serpentine [18], mountain leather asbestos [19] as well as from aluminosilicates and bauxite [20]. Among the raw materials that may be used for non-oxides production, diatomaceous earth shows some advantages such as low price, high specific surface area, high silica content.

By our best knowledge, carbon cryogel was used for the first time as carbon precursor for in situ synthesis of mixture of non-oxide powders ( $\text{Si}_3\text{N}_4$ /SiC). Porous carbon, due to its high surface area and pore accessibility, excellent thermal and chemical stability, as well as, good electrical conductivity is an extremely attractive and competitive material for application in separation technologies. Carbon aerogels and cryogels are a special class of porous carbon materials [1-5] which are usually formed from the sol-gel polycondensation of resorcinol and formaldehyde, followed by supercritical or freeze drying, and subsequent pyrolysis. These materials have a high specific surface and mesoporous structure and we consider that, in combination with diatomaceous earth will represent suitable carbon precursors for in situ synthesis of a mixture of non-oxide powders ( $\text{Si}_3\text{N}_4$ /SiC).

Carbon black has already been successfully used as a carbon precursor for obtaining pure SiC and  $\text{Si}_3\text{N}_4$  [1-3].

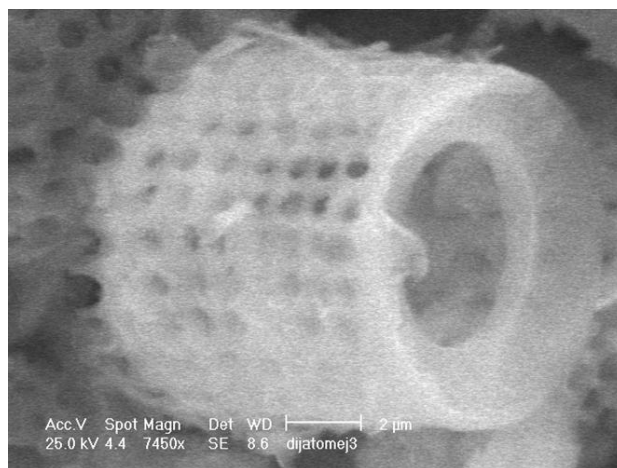
## 2. Experimental

### 2.1. Starting materials

According to the shape and morphology the as-received raw material belongs to the Aulacoseira type of diatoms [21]. A SEM image of a single frustule of the as-received raw material is shown in Fig. 1. The frustule has a capsule-shaped form with a middle circular opening. Regularly spaced rows of the fine pores run along cylindrical walls. They possess a pitted surface area with fine pores of dimensions ranging from the micro scale to the nanometer scale. Its XRD pattern shows that the main mineralogical component is cristoballite ( $\text{SiO}_2$ ) accompanied by an amorphous phase [1]. The chemical composition shows that diatomaceous earth is mainly composed of  $\text{SiO}_2$  and important quantities of  $\text{Al}_2\text{O}_3$ . Also other impurities such as  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3$  are present. However, it is known that the  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  are largely lost at the carbothermal reduction stage. On the other side, it would be expected that  $\text{Fe}_2\text{O}_3$  would be reduced to Fe or to iron silicates ( $\text{FeSiO}_3$ ). In addition it should be mentioned that small quantities of iron help initialize nitridation [22]. Chemical

analyses of obtained powders were performed by means of a PANalytical's - Axios type X-ray fluorescence spectrometer with automated sample feed.

The specific surface area was determined with the BET method.



**Fig. 1** SEM image of a single frustule of as-received diatomaceous earth.

The raw material used was a diatomaceous earth of Serbian origin (Kolubara, basin). In order to reduce the impurity content in the raw material, diatomaceous earth was previously acid treated with a 1 mol dm<sup>-3</sup> concentration HCl solution. The chemical composition of as-received and chemically treated diatomaceous earth are determined by wet chemical methods (Tab. I).

**Tab. I.** Chemical composition of as-received diatomaceous earth and the chemically treated diatomite.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	L.O.I. (1000°C)	Sample
73.68	12.28	3.29	0.72	0.44	1.01	0.12	8.26	As-received
76.58	11.34	1.72	1.22	0.44	0.9	0.11	7.13	Chem. treated

After purification, the content of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> was reduced.

As mentioned above, three different sources of carbon were used for carbothermal reduction: sucrose (i.e. saccharose, C<sub>11</sub>H<sub>22</sub>O<sub>11</sub>, Alfa Aesar, p.a.), carbon cryogel and carbon black. Carbon cryogel was obtained by pyrolyzing RF cryogels in an inert atmosphere as described elsewhere [23]. We used carbon black which is a domestic inexpensive raw material (Miloje Zakić-Kruševac). All reducing agents were over 99% pure.

## 2.2. Preparation of mixtures

Mixtures of diatomaceous earth with different reducing agents: sucrose, carbon cryogel and carbon black, in the further text, will be denoted as mixtures I, II and III.

Mixture I was obtained by dissolving sucrose with an appropriate solvent (sucrose/distilled H<sub>2</sub>O) using a magnetic stirrer. Diatomaceous earth was soaked in this solution containing a carbon precursor (sucrose), homogenized with a magnetic stirrer and

dried until total vaporization of distilled H<sub>2</sub>O at 383 K. Starting mixture I, was obtained after carbonization at 1273 K in nitrogen flow for 4 h. Mixtures I-III of constant molar C/SiO<sub>2</sub> mol ratio (5/1) were homogenized by vibro-milling for 2 h in the presence of distilled water.

The green bodies were held in a graphite boat which was placed in an alumina reactor of an atmosphere-controlled tube furnace in nitrogen flow. Heat treatment was at temperatures between 1523 and 1823 K for 1, 2 and 4 h. The nitrogen gas used contained less than 5 ppm O<sub>2</sub> and H<sub>2</sub>O. In all experiments a N<sub>2</sub> flow of 0.05 l·min<sup>-1</sup> was used.

The nitrogen flow was kept during cooling till 473 K. The excess carbon of the reaction products was removed from samples by oxidation in air at 973 K for 4 hours.

### 2.3. Characterization of powder mixtures

Specific surface area, S<sub>BET</sub> was calculated using the gravimetric McBain method.

The reaction products were analyzed by XRD over the 2θ range from 10° up to 80° using a diffractometer with CuKα as the target. XRD was also used to evaluate crystalline size of the SiC and Si<sub>3</sub>N<sub>4</sub> phases. Before measuring angular correction was done by a high quality Si standard. The average crystalline size, <D>, was calculated from Scherer's formula [24]:

$$\langle D \rangle = 0.9 \cdot \lambda \cdot (\beta_{1/2} \cdot \cos\theta)^{-1}$$

where λ is the wavelength of the X-rays, θ is the Bragg angle of the crystal face (hkl), β = (β<sub>m</sub><sup>2</sup> - β<sub>s</sub><sup>2</sup>), β is the corrected half width, β<sub>m</sub> is the observed half width and β<sub>s</sub> is the half width of the standard Si sample.

Micrographs were obtained with a Philips scanning electron microscope (SEM) at 30 kV accelerating voltage.

### 3. Results and discussion

Tab. II shows BET specific surface areas and mean particle size of starting mixtures. It can be seen that BET specific surface areas as well as mean particle size vary depending on the reducing agent. In spite of the much lower specific surface area of carbon black mixture III has the smallest mean particle size and the highest specific surface area.

**Tab. II.** Specific surface areas and mean particle size

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	Mean particle size (μm)
I	141	23.8
II	263	22.7
III	364	8.6
Diat.earth (acid treat.)	7	30

Tab. III shows the evolution of the crystalline phases formed as a function of the reaction temperature for a constant heating time, 4h.

Cristobalite (SiO<sub>2</sub>) as the major phase decreases with increasing temperature and it finally disappears at 1723 K in all three mixtures, followed by SiC and Si<sub>2</sub>N<sub>2</sub>O appearance. This behavior can be explained by its consuming for SiC and Si<sub>2</sub>N<sub>2</sub>O phases formation. Appearance of the Si<sub>2</sub>N<sub>2</sub>O phase (sinoite) is based on the reaction (1)



which involves vapor phases of SiO and N<sub>2</sub> and gives a powdery Si<sub>2</sub>N<sub>2</sub>O. Appearance of the Si<sub>2</sub>N<sub>2</sub>O phase indicates that prior to the reaction (1) a carbothermal-reduction of SiO<sub>2</sub> occurred according to reactions (2):



Also, the presence of SiC is common to all three mixtures at this temperature. Formation of this final product can be explained by equations given elsewhere [3].

The Si<sub>3</sub>N<sub>4</sub> phase first appeared after 2 h soaking time, in the sample containing sucrose and carbon black as reducing agents at 1623 K. This can be explained with the fact that mixture III has the highest specific surface (table II) and hence the largest number of contacts which accelerate the reaction (which is beneficial for the further course of the reaction). Also, mixture I was obtained from a solution. In other words, the carbon precursor was introduced via a solution which allowed its penetration in all free space in diatomaceous earth particles.

At 1723 K, β-Si<sub>3</sub>N<sub>4</sub> is the principle phase in all mixtures. Also, at this temperature, α-Si<sub>3</sub>N<sub>4</sub> should be produced, but the presence of impurities in starting materials produced liquid due to low temperature eutectic reactions which favor the formation of β-Si<sub>3</sub>N<sub>4</sub> instead of α-Si<sub>3</sub>N<sub>4</sub> [25].

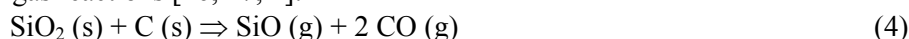
**Tab. III.** The phase evolution of the crystalline phases after heat treatment at 1523 K to 1823 K for 4 h.

Sample Reducing agent	Reaction temperature (K)	Crystalline phases
sucrose	1523	SiO <sub>2</sub>
sucrose	1623	SiC, Si <sub>3</sub> N <sub>4</sub> , Si <sub>2</sub> N <sub>2</sub> O
sucrose	1723	SiC, Si <sub>3</sub> N <sub>4</sub>
sucrose	1823	SiC
carbon black	1523	SiO <sub>2</sub> , Si <sub>2</sub> N <sub>2</sub> O, FeSiO <sub>3</sub>
carbon black	1623	SiC, Si <sub>3</sub> N <sub>4</sub> , Si <sub>2</sub> N <sub>2</sub> O
carbon black	1723	SiC, Si <sub>3</sub> N <sub>4</sub>
carbon black	1823	SiC
carbon cryogel	1523	SiO <sub>2</sub>
carbon cryogel	1623	SiO <sub>2</sub> , Si <sub>2</sub> N <sub>2</sub> O
carbon cryogel	1723	Si <sub>2</sub> N <sub>2</sub> O, SiC, Si <sub>3</sub> N <sub>4</sub>
carbon cryogel	1823	SiC

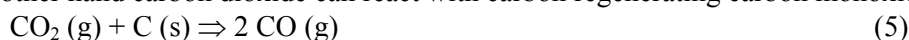
However, at 1823 K the Si<sub>3</sub>N<sub>4</sub> phase is unstable in the presence of CO according to the reaction:



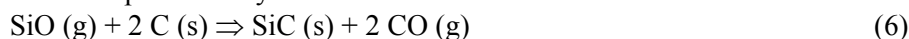
Thus, CO (g) is responsible for decreasing of the Si<sub>3</sub>N<sub>4</sub> phase. There are two sources of CO (g) for generating reaction (1); first are reactions (4), (5) and (6) and the second is oxygen impurity in the nitrogen gas used. Formation of SiC requires a series of solid-solid, solid-gas and gas-gas reactions [26, 27, 1]:



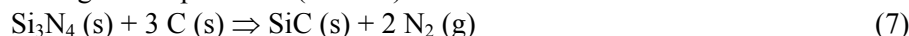
On the other hand carbon dioxide can react with carbon regenerating carbon monoxide:



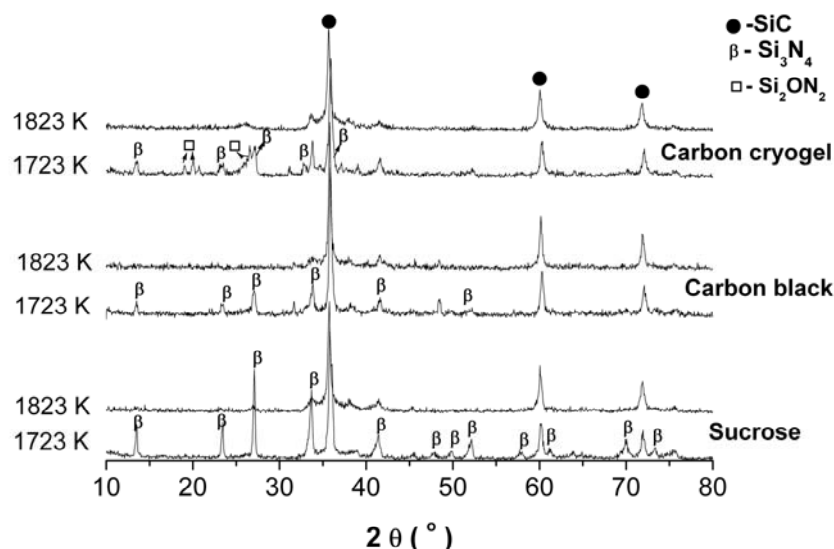
Silicon carbide is produced by the reaction between silicon monoxide and solid carbon:



Industrially pure nitrogen gas contains 0.05 Pa oxygen. When  $O_2$  (g) reacts with C (s) in the furnace, 0.1 Pa CO (g) is generated [27]. Also the reaction between  $Si_3N_4$  and C often proceeds at higher temperatures (1823 K):



These two reactions are responsible for the disappearing of the  $Si_3N_4$  phase from powders at high temperatures. Fig. 2 shows that almost the complete amount of the  $Si_3N_4$  phase is converted into SiC at 1823 K.



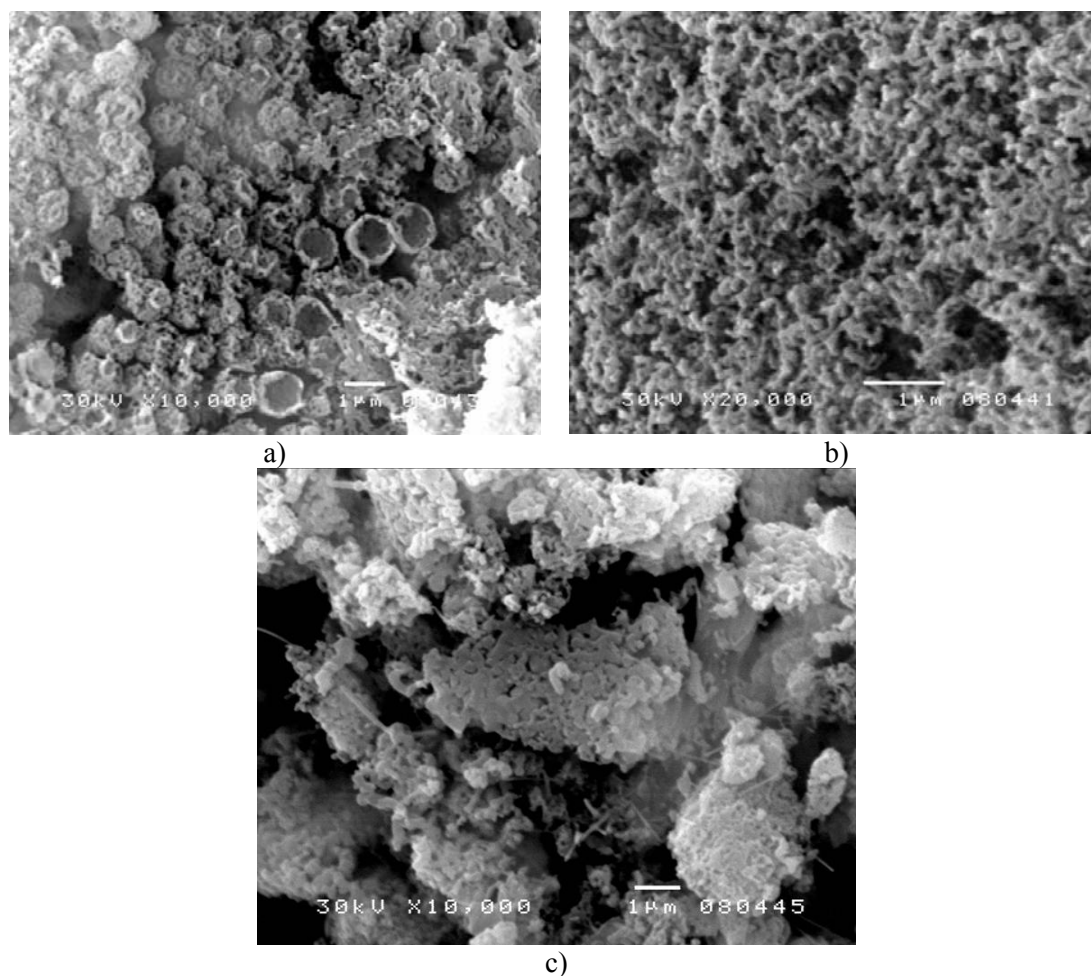
**Fig. 2** XRD patterns of samples after heat treatment at 1723 and 1823 K for 4h.

In the XRD patterns all peaks are broadened since ultra fine crystals were obtained. The estimated crystalline sizes of samples with the Sheerer formula [24] confirmed that the average crystalline size lies in the nano range (Tab. IV).

**Tab. IV.** Average crystalline size (nm) for different sources of carbon at 1823 K for 4h.

Reducing agent		SiC	$Si_3N_4$	$Si_2ON_2$
Sucrose	1723 K	24	30	
	1823 K	24		
Carbon cryogel	1723 K	24	30	41
	1823 K	30		
Carbon black	1723 K	37	44	
	1823 K	44		

SEM micrographs of samples obtained after 4 h at 1723 K are given in Fig. 3. The morphology of obtained powders shows that they are highly aggregated and composed of nano particles. The morphology of all three powders obtained show that these products retain characteristics of some fragments of the original diatomite similar to a honeycomb (reducing agent: sucrose) and a sponge-like microstructure (in the case of carbon cryogel and carbon black as reducing agent).



**Fig. 3** SEM micrograph of powders obtained after 4 h at 1723 K using (a) sucrose as reducing agent (b) carbon cryogel and (c) carbon black.

According these results the best phase compositions were obtained at 1450° C for 4 h, due to the presence of the both nitride and carbide phases. Chemical analysis was performed as well as the measurements of the specific surface area of the obtained powders at this temperature (Tab. V).

**Tab. V.** Chemical analysis and specific surface area of powders obtained at 1450° C for 4 h.

	Si	Al	N	C	O	Fe	Ca	Mg	K	Na	S <sub>BET</sub> (m <sup>2</sup> /g)
<b>I</b>	53.1	11.1	19.8	10.4	2.3	0.8	0.9	0.3	0.7	0.6	21.3
<b>II</b>	54.3	11.1	18.6	11.3	1.9	0.7	0.8	0.2	0.6	0.5	20.8
<b>III</b>	54.4	11.1	16.6	12.6	2.2	0.8	0.9	0.2	0.6	0.6	19.9

Obviously the chemical compositions have changed during carbothermal-nitridation reactions. The highest loss is in iron content, which reduced to a value less than 1 mas %.

These powders can be used as raw materials for industrial application, especially in metallurgy where high purity of powders is not so important.

#### 4. Conclusions

This study demonstrated that it is feasible to produce inexpensive non oxide powders using diatomaceous earth waste.

Carbonitriding of diatomaceous earth in low nitrogen flow rate leads to the formation of  $\text{Si}_3\text{N}_4/\text{SiC}$  composite powders. According to XRD analyses, the temperature of 1723 K appears to be the proper condition for the synthesis of  $\text{Si}_3\text{N}_4/\text{SiC}$  composite powders. The reaction products depend on the reaction temperature and reducing agent (i.e. carbon source), whereby intermediate compounds appear in small quantities. With increasing temperature, the amount of SiC increases compared to silicon nitride. Powders obtained at higher temperature (1723 K) are the mixture of silicon carbide and silicon nitride. Results also show that all powders are nanometric in size. The average crystallite size of  $\text{Si}_3\text{N}_4$  and SiC is in range 25-45 nm.

#### Acknowledgement

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**Садржај:** У овом раду приказани су резултати испитивања синтезе неоксидних прахова применом карботермалне редукције и нитрирања дијатомејске земље, која представља отпад приликом експлоатације угља. Основни мотив био је да се испита потенцијална могућност коришћења дијатомејске земље као главног прекурсора приликом синтезе јефтиних неоксидних прахова као и да решимо еколошко питање отада. Такође у раду је проучаван утицај угљеничних материјала (карбонизоване сахарозе, угљеничног криогела, активног угља) који су коришћени као редукционо средство на ток синтезе и особине добијених неоксидних прахова. Прахови су окарактерисани помоћу рендгенске дифракционе анализе и скенирајуће електронске микроскопије. Утврђено је да се овим поступком коришћењем дијатомејске земље добијају фазе које одговарају смеши неоксидних прахова ( $\text{Si}_3\text{N}_4/\text{SiC}$ ) или чист прах  $\text{SiC}$  у зависности од температуре синтезе.

**Кључне речи:** Реакције гас-чврсто стање, микроструктура, рентгенска дифракција, скенирајућа електронска микроскопија.

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